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Method for production of trichlorosilane and silicon for use in the production of trichlorosilane.

Title of Invention

Method for production of trichlorosilane and silicon for use in the production of trichlorosilane.

Field of Invention

- 5 The present invention relates to a method for the production of trichlorosilane by reaction of silicon by HCl gas and to silicon for the use in production of trichlorosilane.

Background Art

- 10 In the method of production of trichlorosilane (TCS), metallurgical grade silicon is reacted with HCl gas in a fluidized bed reactor, in a stirred bed reactor or in a solid bed reactor. The process is generally carried out at a temperature between 250° and 1100°C. In the reaction other volatile silanes than TCS are formed, mainly silicon tetrachloride (STC). Since TCS normally is the preferred product, the selectivity of the reaction given as the molar ratio of TCS/(TCS + other
15 silanes) is an important factor. The other important factor is the reactivity of the silicon, measured as first pass HCl conversion. Preferably more than 90% of HCl is converted to silanes, but industrially lower reactivity can be observed.

- The selectivity and reactivity will depend strongly on the process temperature when silicon and HCl is reacted. According to the equilibrium calculation the
20 amount of TCS should be about 20 – 40% (remaining is mainly STC) in the temperature range given above. However, in practical terms a significantly higher TCS selectivity is observed, and at temperatures below 400°C it is possible to observe TCS selectivity of more than 90%. The reason for this big deviation from equilibrium is that the product composition is given by kinetic
25 limitations (formation of active species on the silicon surface). Higher temperature will move the product distribution towards the equilibrium composition and the gap between the observed selectivity and the calculated selectivity will get smaller. Reactivity will increase with higher temperature. Coarser silicon particles (lumps) can therefore be used when the temperature is
30 increased and still maintaining close to 100% HCl consumption.

Higher pressure will favour a higher TCS selectivity.

Metallurgical grade silicon contains a number of contaminating elements like Fe, Ca, Al, Mn, Ni, Zr, O, C, Zn, Ti, B, P and others. Some contaminants will either be inert to HCl like Fe and Ca and will form solid, stable compounds like FeCl_2 and CaCl_2 . The stable metal chlorides, will depending on their size, either be
5 blown out of the reactor with the silane or be accumulated in the reactor. Other contaminants like Al, Zn, Ti, B and P form volatile metal chlorides, which leave the reactor together with the silanes produced.

O and C are enriched in slag particles of the silicon that do not react or react very slowly with HCl and tend to accumulate in the reactor. The smallest slag
10 particles can be blown out of the reactor and trapped in the filter systems.

Many of the contaminants in metallurgical grade silicon influences the performance of the silicon in the process of producing trichlorosilane by reaction of silicon with HCl gas. Thus both the reactivity of the silicon and the selectivity can be effected both positively and negatively.

15 Particularly, it is known that metallurgical silicon having an increased content of phosphorus very negatively effects both the reactivity and the selectivity of the process. It is thus preferred to use metallurgical grade silicon having a very low phosphorus content. Such low phosphorus containing silicon is, however, costly to produce as this requires a thorough selection of raw materials as to their
20 phosphorus content.

Disclosure of Invention

It has now been found that silicon having an increased chromium content provide a high selectivity when used in the method for the production of trichlorosilane by reaction with HCl. It has further been found that if the
25 chromium content in the trichlorosilane reactor is controlled within certain limits an increase in selectivity is obtained.

According to a first aspect, the present invention relates to a method for the production of trichlorosilane by reaction of silicon with HCl gas at a temperature between 250° and 1100°C and a pressure of 1 – 30 atm in a fluidized bed
30 reactor, in a stirred bed reactor or in a solid bed reactor, which method is

characterised in that the silicon supplied to the reactor contains between 50 and 10 000 ppm of chromium.

Preferably the silicon supplied to the reactor contains 75 to 1000 ppm chromium.

- 5 The chromium is alloyed with the silicon, is mechanically mixed with the silicon or is added to the reactor separately.

According to a second aspect, the present invention relates to a silicon for the use in the production of trichlorosilane by reaction of silicon with HCl gas, where the silicon contains between 50 and 10 000 ppm chromium, the remaining
10 except for normal impurities being silicon.

The silicon according to the present invention is produced in conventional way in carbothermic reduction furnaces. The chromium content in the silicon can either be regulated and controlled by selection of raw materials, adding chromium to the furnace, using electrodes containing chromium or chromium may be added
15 to molten silicon in the ladle after the silicon has been tapped from the reduction furnace.

It has surprisingly been found that the addition of chromium to silicon improves the selectivity of TCS in the process of producing trichlorosilane.

According to a third aspect the present invention relates to a method for the
20 producing of trichlorosilane by reaction of silicon with HCl gas at a temperature between 250° and 1100° C and a pressure of 1 – 30 atm in a fluidized bed reactor, in a stirred bed reactor or in a solid bed reactor, which method is characterised in that chromium is added to the reactor in an amount necessary to control a chromium content in the reactor of between 200 and 50 000 ppm
25 based on the weight of silicon in the reactor.

Preferably chromium is supplied to the reactor in an amount necessary to control a chromium content in the reactor of between 250 and 25 000 ppm.

Short description of the drawings

Figure 1 and 2 show diagrams for selectivity of TCS produced from commercial available silicon samples in a fixed bed reactor at 365°C according to the present invention and compared with the TCS selectivity according to TCS produced according to prior art.

Figure 3 shows a diagram for the selectivity of TCS and HCl conversion of pure silicon alloyed with 550 ppm Cr according to the present invention and compared with the TCS selectivity using pure silicon.

Figure 4 shows a diagram for selectivity of TCS produced from a commercial available silicon sample in a continuous fluid bed reactor at 365°C according to the present invention and compared with the TCS selectivity according to TCS produced according to prior art.

Figure 5 show diagram for selectivity of TCS produced from commercial available silicon samples in a fixed bed reactor at 515°C according to the present invention and compared with the TCS selectivity according to TCS produced according to prior art.

Detailed description of the invention

The following examples 1 to 3 were all carried out in a laboratory fixed-bed reactor made from quartz and embedded in a heated aluminum block. The temperature of the heating block was kept at 350°C which gives a temperature in the reactor of 365°C. For each test 1 gram of silicon having a particle size of between 180 and 250 μm was added to the quartz reactor. A mixture of HCl and argon in an amount of 10 ml/min each was supplied to the reactor. The composition of the product gas from the reactor was measured with a GC. Selectivity was measured as $\text{TCS}/(\text{TCS} + \text{other silanes})$ and reactivity was measured as HCl conversion; that is the amount of HCl used in the reaction.

The following example 4 was carried out in a laboratory fluidized-bed reactor made from steel and embedded in a heated aluminum block. The reactor is started up with 5 gram of silicon having a particle size of between 180 and 250 μm . A mixture of HCl and are in amounts of 280 ml/min and 20 ml/min
5 respectively was supplied to the reactor. The temperature of the reactor is maintained at 325°C during the run. As the reaction proceeds new silicon is added semi-continuously from the top of the reactor to maintain a total amount of 5 grams inside the reactor. The composition of the product gas from the reactor was measured with a GC. Selectivity was measured as TCS/(TCS +
10 other silanes) and reactivity was measured as HCl conversion; that is the amount of HCl used in the reaction.

The following example 5 was carried out in a laboratory fixed-bed reactor made from quartz and embedded in a heated aluminum block. The temperature of the
15 heating block was kept at 500°C which gives a temperature in the reactor of 515°C. For each test 1 gram of silicon having a particle size of between 180 and 250 μm was added to the quartz reactor. A mixture of HCl and argon in an amount of 10 ml/min each was supplied to the reactor. The composition of the product gas from the reactor was measured with a GC. Selectivity was
20 measured as TCS/(TCS + other silanes) and reactivity was measured as HCl conversion; that is the amount of HCl used in the reaction.

Example 1

25 Metallurgical grade silicon produced by Elkem ASA, were prepared by melting the silicon adding phosphorus to the silicon to provide silicon containing 150 ppmw of phosphorus. The solidified phosphorus-containing silicon was crushed
— and milled to a particle size between 180 and 250 μm . 1 % by weight of chromium powder was added to a part of the phosphorus-containing silicon.
30 Thus it was made two samples of phosphorus-containing silicon; sample A containing 1 % by weight of chromium and sample B containing no chromium except for minor impurity.

The chemical analysis of silicon samples A and B are shown in Table 1. Table 1.

	Sample A	Sample B
Si %	98.26	99.26
Al %	0.113	0.113
Ca %	0.002	0.002
Fe %	0.308	0.308
Zr ppmw	11	11
Sr ppmw	< 5	< 5
Pb ppmw	< 5	< 5
Bi ppmw	< 5	< 5
As ppmw	< 5	< 5
Zn ppmw	< 5	< 5
Cu ppmw	11	11
Ni ppmw	9	9
Mn ppmw	82	82
Cr	1 % by weight	13 ppmw
V ppmw	13	13
Ba ppmw	< 5	< 5
Ti ppmw	227	227
Mo ppmw	19	19
Sb ppmw	< 5	< 5
Sn ppmw	< 5	< 5
K ppmw	< 5	< 5
P ppmw	150	150

- 5 Samples A and B were used to produce trichlorosilane in a laboratory fixed-bed reactor described above. Two parallel runs were made with sample B. The selectivity for TCS produced from samples A and B are shown in Figure 1.

As can be seen from Figure 1, the addition of 1 % by weight of chromium to the phosphorus-containing silicon resulted in a substantial increase in selectivity.

- 10 100% of the HCl was converted in these runs.

Example 2

Siligrain® silicon produced by Elkem ASA was screened to a particle size between 180 and 250 µm. 0,3 and 1 % by weight of chromium powder was added to a part of the silicon. Thus it was made three samples of Siligrain® silicon sample C containing 1 % by weight of chromium, sample D containing 0,3 % by weight of chromium and sample E containing no chromium except for minor impurity.

10 The chemical analysis of silicon samples C, D and E are shown in Table 2.

Table 2

	Sample C	Sample D	Sample E
Si %	98.28	98.98	99.28
Al %	0.232	0.232	0.232
Ca %	0.019	0.019	0.019
Fe %	0.154	0.154	0.154
Zr ppmw	38	38	38
Sr ppmw	< 5	< 5	< 5
Pb ppmw	< 5	< 5	< 5
Bi ppmw	< 5	< 5	< 5
As ppmw	< 5	< 5	< 5
Zn ppmw	< 5	< 5	< 5
Cu ppmw	<5	<5	<5
Ni ppmw	<5	<5	<5
Mn ppmw	15	15	15
Cr	1 % by weight	0,3% by weight	11 ppmw
V ppmw	12	12	12
Ba ppmw	< 5	< 5	< 5
Ti ppmw	164	164	164
Mo ppmw	15	15	15
Sb ppmw	< 5	< 5	< 5
Sn ppmw	< 5	< 5	< 5
K ppmw	< 5	< 5	< 5
P ppmw	24	24	24

Samples C, D and E were used to produce trichlorosilane in a laboratory fixed-bed reactor described above. Two parallel runs were made with sample E. The selectivity for TCS produced from samples C, D and E are shown in Figure 2.

5 As can be seen from Figure 2, the addition of 0,3 and 1 % by weight of chromium to Silgrain® silicon resulted in a substantial increase in selectivity. 100% of the HCl was converted in these runs.

Example 3

10 Pure silicon (polysilicon grade) having a very low content of impurities was alloyed with 550 ppm chromium. The chromium alloyed silicon was used to produce trichlorosilane using the reactor and the method described above. As shown in Figure 3, the selectivity was higher in the sample with alloyed chromium. 100% of the HCl was converted in these runs.

Example 4

15 Metallurgical grade silicon produced by Elkem ASA (sample F) was crushed and milled to a particle size between 180 and 250 µm. The composition of the sample is given in Table 3. Sample F was used to produce trichlorosilane in a laboratory fluidised-bed reactor described above. Two parallel runs were made,
20 but in the second run 2% by weight (0,1025 gram) of Cr was added separately to the reactor when about 33 grams of silicon was consumed. The selectivity for TCS produced from sample F with and without Cr addition is shown in Figure 4.

As can be seen from Figure 4, the addition of 2 % by weight of chromium to the silicon resulted in about 3% absolute increase in selectivity. 100% of the HCl
25 was converted in these runs.

Table 3

	Sample F
Si %	99.24
Al %	0.120
Ca %	0.014
Fe %	0.306
Zr ppmw	6
Sr ppmw	< 5
Pb ppmw	< 5
Bi ppmw	< 5
As ppmw	< 5
Zn ppmw	< 5
Cu ppmw	12
Ni ppmw	14
Mn ppmw	82
Cr ppmw	11
V ppmw	23
Ba ppmw	< 5
Ti ppmw	228
Mo ppmw	8
Sb ppmw	< 5
Sn ppmw	< 5
K ppmw	< 5
P ppmw	17

Example 5

5

Metallurgical grade silicon produced by Elkem ASA was crushed and milled to a particle size between 180 and 250 μm . 0,54 % by weight of chromium powder was added to a part of the silicon. Thus it was made two samples of silicon, sample H containing 0,54 % by weight of chromium and sample G containing no chromium except for minor impurity.

10

The chemical analysis of silicon samples G and H are shown in Table 4.

Table 4

	Sample G	Sample H
Si %	97,68	97,14
Al %	0,132	0,132
Ca %	0,002	0,002
Fe %	1,813	1,813
Zr ppmw	147	147
Sr ppmw	<5	<5
Pb ppmw	<5	<5
Bi ppmw	<5	<5
As ppmw	<5	<5
Zn ppmw	10	10
Cu ppmw	42	42
Ni ppmw	33	33
Mn ppmw	95	95
Cr	36 ppm	0,54% by weight
V ppmw	86	86
Ba ppmw	34	34
Ti ppmw	769	769
Mo ppmw	10	10
Sb ppmw	11	11
Sn ppmw	<5	<5
K ppmw	<5	<5
P ppmw	56	56

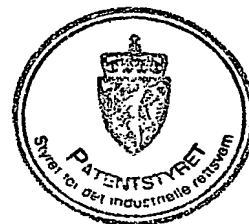
Samples G and H were used to produce trichlorosilane in a laboratory fixed-bed reactor described above. The selectivity for TCS produced from samples G and H are shown in Figure 5. Compared to examples 1 to 4, higher temperature in the reactor reduced the selectivity significantly, but as can be seen from Figure 5, the addition of 0,54 % by weight of chromium to the silicon resulted in about 15-20% absolute increase in selectivity. 100% of the HCl was converted in these runs.



Claims:

1. Method for the production of trichlorosilane by reaction of silicon with HCl gas at a temperature between 250° and 1100°C, and a pressure of 1-30 atm in a fluidized bed reactor, in a stirred bed reactor or in a solid bed reactor, c h a r a
5 c t e r i z e d i n that the silicon supplied to the reactor contains between 50 and 10 000 ppm chromium.
2. Method according to claim 1, c h a r a c t e r i z e d i n that the silicon supplied to the reactor contains between 75 and 1000 ppm chromium.
3. Method according to claim 1 or 2, c h a r a c t e r i z e d i n that
10 chromium is alloyed with the silicon.
4. Method according to claim 1 or 2, c h a r a c t e r i z e d i n that chromium is mechanically mixed with the silicon before the silicon is supplied to the reactor or added separately to the reactor.
5. Silicon for use in the production of trichlorosilane by reaction of silicon
15 with HCl gas, c h a r a c t e r i z e d i n that the silicon contains between 50 and 10 000 ppm chromium, the remaining except for normal impurities being silicon.
6. Silicon according to claim 5, c h a r a c t e r i z e d i n that the silicon contains between 75 and 1000 ppm chromium.
7. Silicon according to claim 5 or 6, c h a r a c t e r i z e d i n that chromium
20 is alloyed with the silicon.
8. Silicon according to claim 5 or 6, c h a r a c t e r i z e d i n that chromium is mechanically mixed with the silicon.
9. Method for the production of trichlorosilane by reaction of silicon with HCl
25 gas at a temperature between 250 and 1100°C, and a pressure of 1-30 atm in a fluidized bed reactor, in a stirred bed reactor or in a solid bed reactor, c h a r a c t e r i z e d i n that chromium is supplied to the reactor in an amount necessary to control a chromium content in the reactor of between 200 and 50 000 ppm based on the weight of silicon in the reactor.

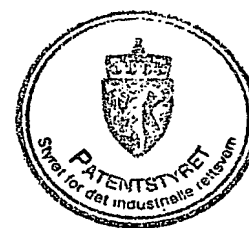
10. Method according to claim 9, characterized in that chromium is supplied to the reactor in an amount necessary to control the chromium content in the reactor between 250 and 25000 ppm chromium.
- 5 11. Method according to claim 9, characterized in that chromium supplied to the reactor is alloyed with the silicon.
12. Method according to claim 9, characterized in that chromium supplied to the reactor is mechanically mixed with the silicon before the mixture is supplied to the reactor.
- 10 13. Method according to claim 9, characterized in that chromium and silicon are added separately to the reactor.



ABSTRACT

The present invention relates to a method for the production of trichlorosilane by reaction of silicon with HCl gas at a temperature between 250° and 1100°C, and
5 a pressure of 1-30 atm in a fluidized bed reactor, in a stirred bed reactor or a solid bed reactor, where the silicon supplied to the reactor contains between 50 and 10.000 ppm chromium.

The invention further relates to silicon for use in the production of trichlorosilane by reaction of silicon with HCl gas, containing between 50 and 10.000 ppm
10 chromium, the remaining except for normal impurities being silicon.



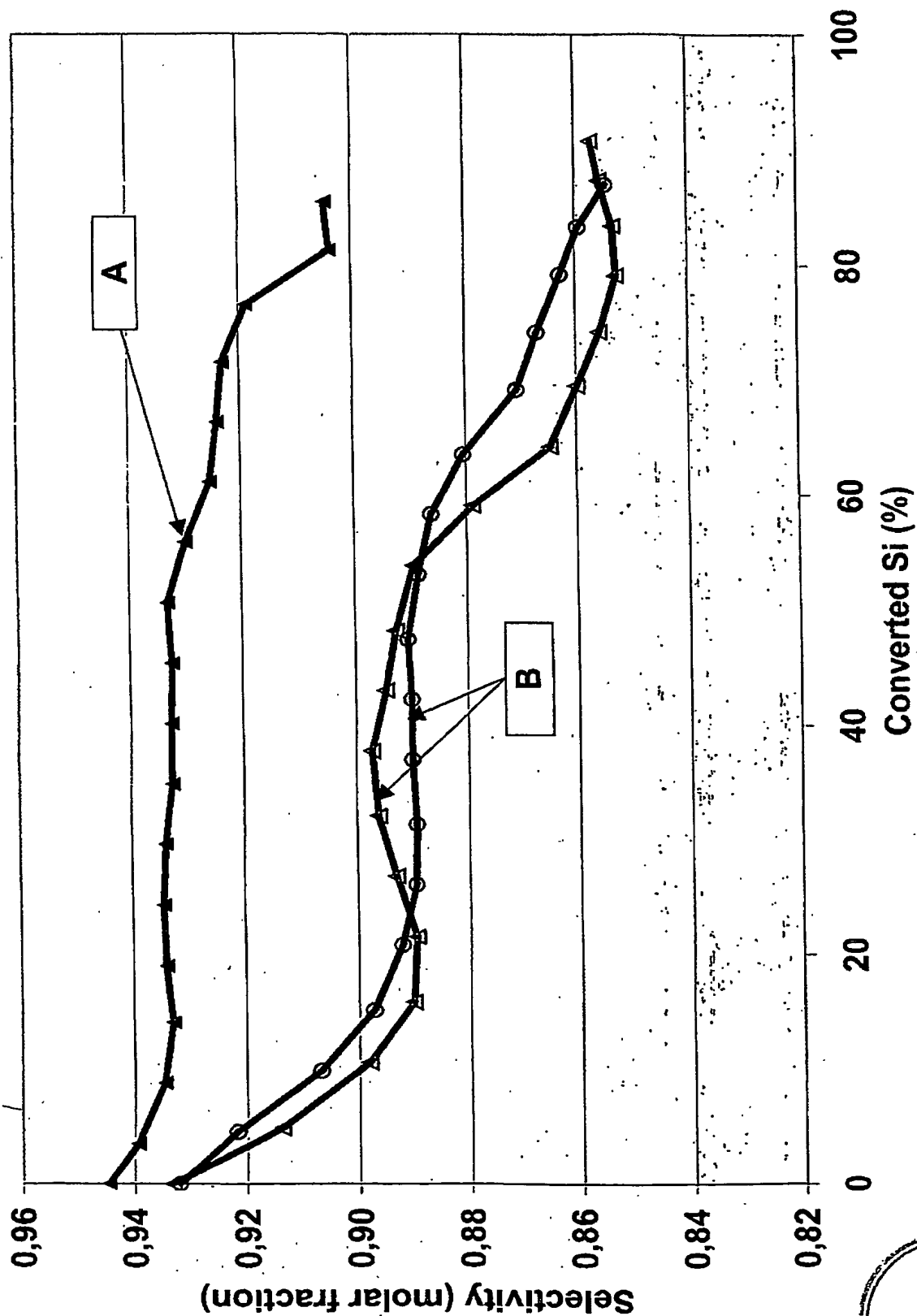
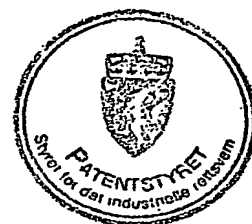


Figure 1



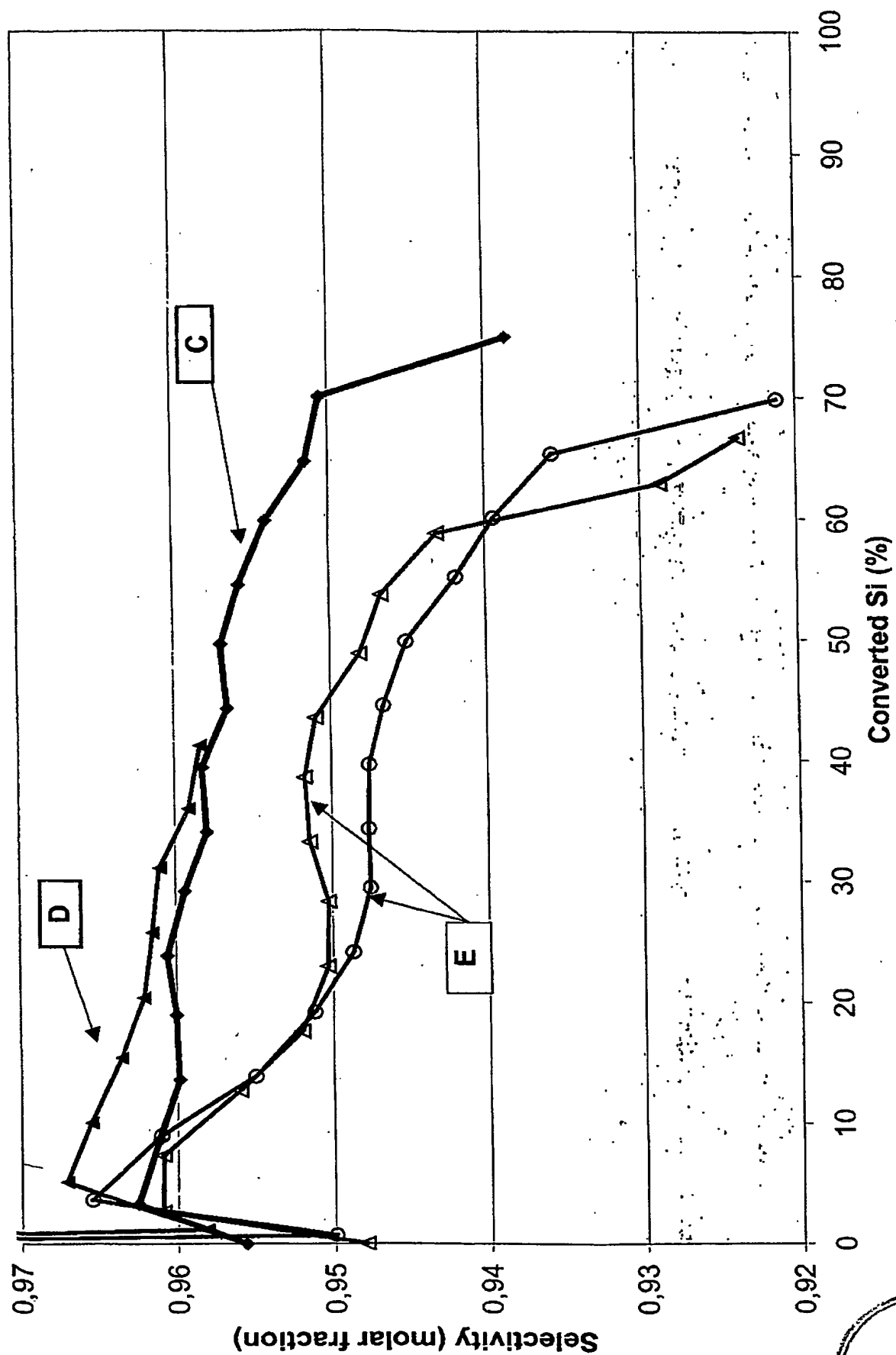


Figure 2



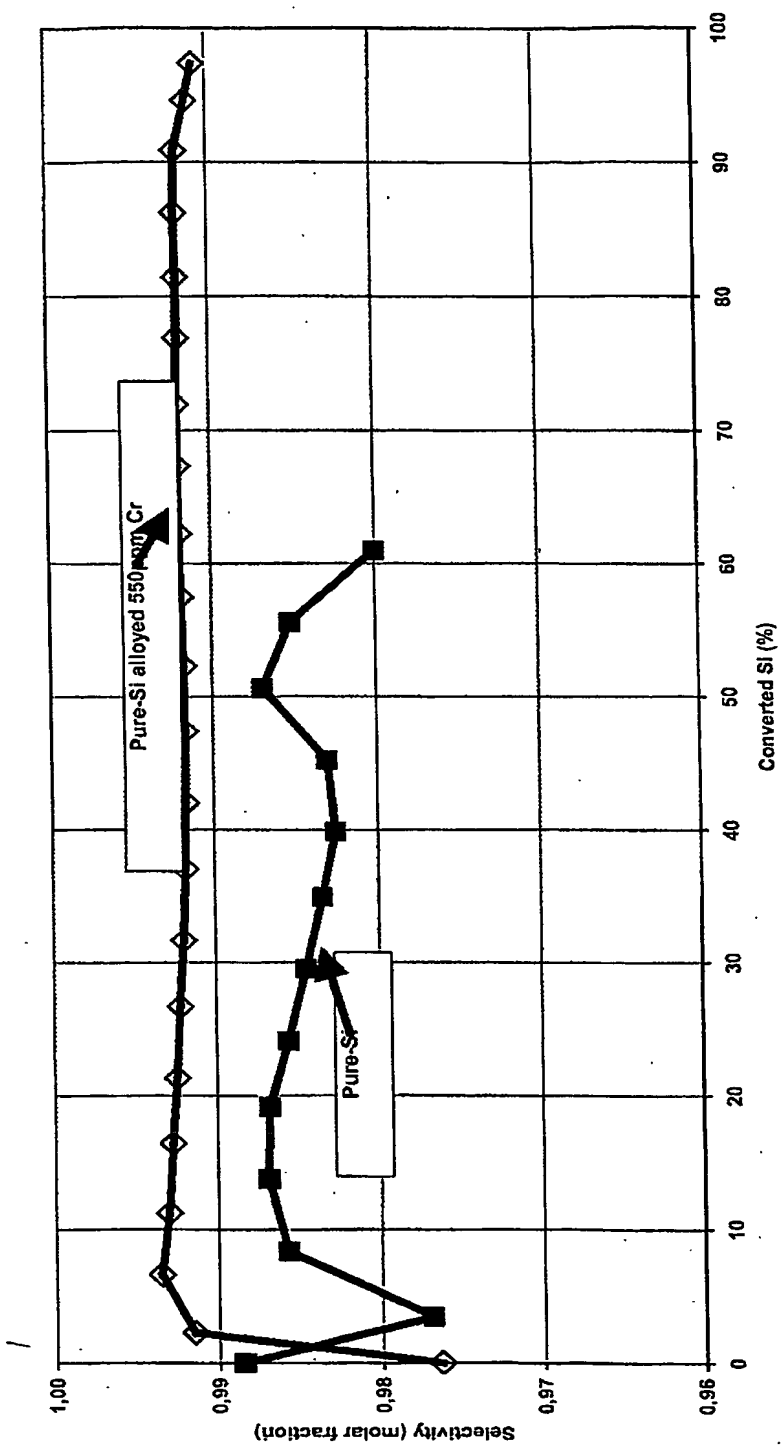


Figure 3



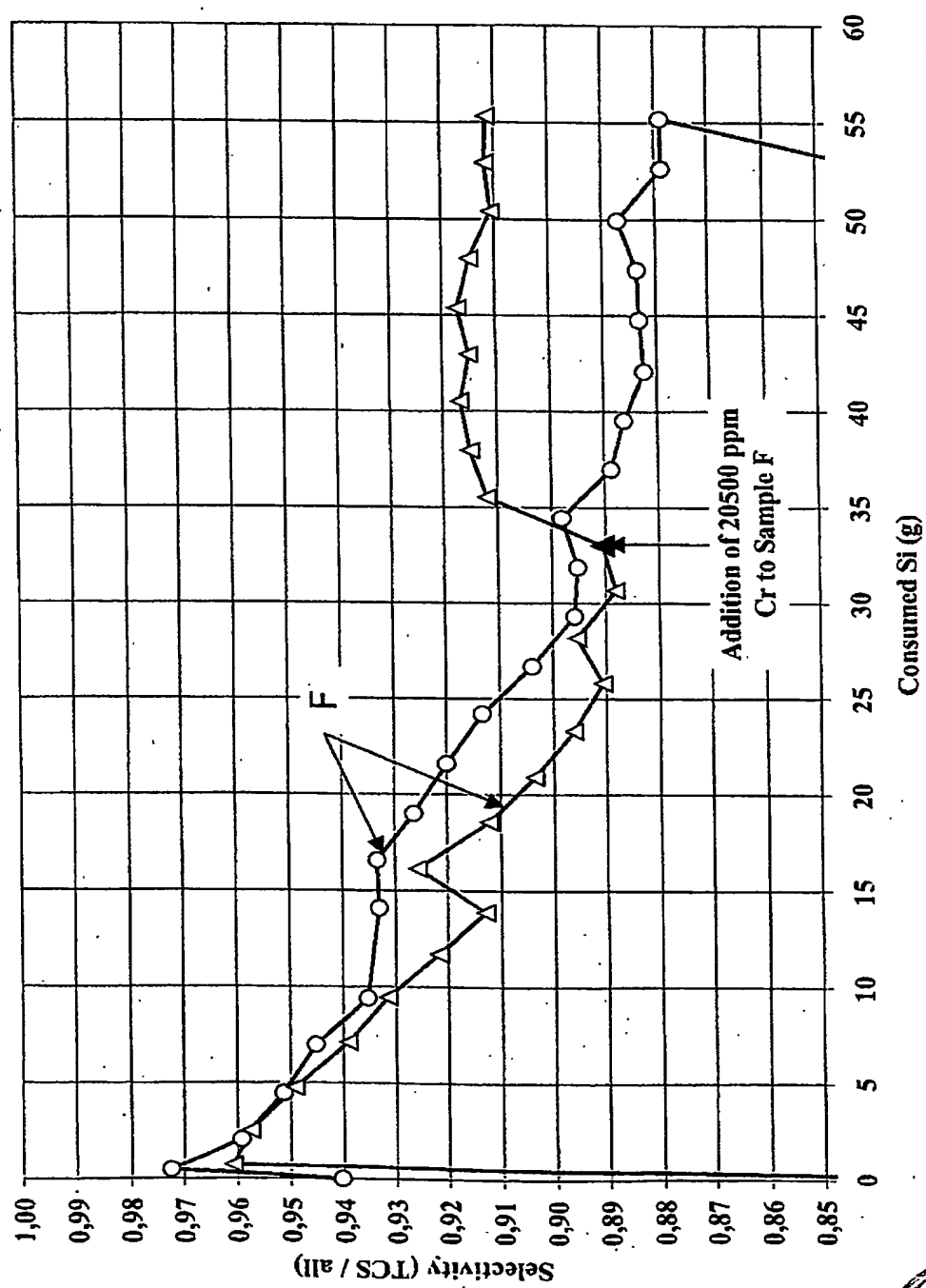


Figure 4



Figure 5

